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Research on Activity Characteristics on Composite Cementitious Materials Based on Phosphogypsum

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Abstract

The physical and chemical characteristics of each of phosphogypsum-based silicon and aluminum composite materials were tested and analyzed. By means of ratio test, it is proved that the range of composite materials' compressive strength is 1.46MPa to 2.78MPa along with the range of the ratio in 1:1:4.7 to1:1:8. The experiments of active characteristics of composite materials were designed in method of activity ratio K_a value, whose results showed that in early stage, a small amount of hazardous substances in composite materials, such as soluble phosphorus, fluorine and so on, will inhibit free proliferation about the activity of SiO_2 and Al_2O_3, while in medium and late stage, the K_a value that showing a inflection point at the age of 28 days has a relationship with the OH^- density in alkaline environment. And temperature, an important factor affecting the K_a value of composite materials, was set 80 °C as an optimal temperature in reactions. In a word, by calculating the K_a value, the degree of activity features affected by the external environment was followed by Temperature>Activation time>Fineness. The research could provide theoretical guidance for large-scale application of utilizing industrial solid waste to fill goaf so that ensure the safety of mines.

Keywords: Phosphogypsum, Composite Materials, Physical and Chemical Properties, Activity Ratio, Active Characteristics

Nomenclature

u_θ	velocity in the direction of (m/s)
A	radius of (m)
B	position of
C	further nomenclature continues down the page inside the text box
Greek symbols	
γ	stoichiometric coefficient
δ	boundary layer thicknesses(m)
Subscripts	
r	radial coordinate

1. Introduction

With the continuous development of phosphate rock resources and the increasing strength of development, it formats amounts of huge goafs that become a major hazard threats to safety of mines production seriously [1]. At the same time, phosphogypsum, as the solid emissions processed and utilized by phosphate rock mines, is also rapidly increasing. There are statistics [2] show that the annual emission of existing phosphogypsum was up to 7.0×10^6 t, which ranking the third place in the world and increasing as a rate of 13% yearly. At present, technology of the phosphogypsum depth development and

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utilization is not yet mature that lead to many problems that most of phosphogypsum was stored in tailing dams besides 10% of was exploited. It will not only pay large investments and high maintenance costs, but also occupant a lot of valuable land resources. The phosphogypsum library, as a "hazardous waste" announced by the State Environmental Protection Administration, is both a major hazard leading to the danger of dam failure and a serious pollution source causing serious pollution to the groundwater.

How effective to governance goaf and disposal of phosphogypsum solid emissions has become a concerned issue for the phosphate rock mines and enterprises need to be resolved urgently. By the literature search, there are not a large-scale and low-cost method of using phosphogypsum effectively in the world and also not an example to fill goaf with phosphogypsum as a cemented filling aggregate. Phosphogypsum is a kind of acid material that is extremely fine, which can not stand alone as filling aggregate. Lots of studies have shown that [3-5] there are some complementary features between fly ash and phosphogypsum in cementitious avtivity and acid-base properties while slag both has the cementitious and activation function so that it will change the filling aggregate characteristics of phosphogypsum and enhance the compressive strength of composite binder if blending fly ash, slag, quicklime and phosphogypsum in a reasonable proportion. This paper will research and analysis the physical and chemical properties and activity characteristics of composite cementitious materials that composed of fly ash, slag, phosphogypsum and quicklime. Research can provide theoretical guidance for large-scale application of utilizing industrial solid waste to fill goaf so that ensure the safety of mines.

2. Analysis on physical-chemical properties and components of composite materials

2.1. *Analysis of physical-chemical properties*

With the help of laser particle size analyzer, the particle size distribution of the phosphogypsum, fly ash and slag can be measured. And their chemical composition can also be measured by SRD. The results are shown in Table 1.

Table1. Physical and Chemical properties of Phosphogypsum, Fly ash and Slag

Sample	SiO_2	Al_2O_3	MgO	CaO	TiO_2	P_2O_5	H_2O^-	Loss	Particle Size
Phosphogypsum	8.15	0.80	0.066	34.31	0.10	0.89	5.24	9.96	49.84um
Fly ash	54.15	32.25	0.79	2.45	1.31	0.33	0.06	1.00	71.08um
Slag	33.93	20.39	7.48	32.38	0.88	0.059	0.16	1.32	27.05um

The table above shows that:

(1) Phosphogypsum is a kind of acid material that is extremely fine, which composed of $CaSO_4{\cdot}2H_2O$ that not only has a retards effect but also can inhibite the early gelling of phosphogypsum consolidation body. The CaO in the chemical composition plays a activated and complementary role in composite materials.

(2) Fly ash, as an alkaline substance which occoured neutral reaction with phosphogypsum, was composed of SiO_2 and Al_2O_3, 54.15% and 32.25% respectively that was provided with the cementation function.

(3) According to the alkaline coefficient formula [6]， we can calculate the alkaline coefficient of slag was 0.73. Slag maked up with SiO_2、 Al_2O_3 and CaO, was classified acid that both has cementitious and activative functions.

In summary, because of extremely fine particles, phosphogypsum can not stand alone as filling aggregate while can occoure neutral reaction with fly ash. Both of them were clay substances, at the same time slag has cementitious and activative functions which can via the ratio experiment let the phosphogypsum stand alone as filling aggregate by means of mixing fly ash, slag and activitor with phosphogypsum in order to change the nature of composite materials.

2.2. *Introduction of composite materials*

Composite materials that composed by phosphogypsum, fly ash, slag and quicklime were tested and analyzed by single and mixture orthogonal experiments, which show that they have good compatibility and stability.

The experiment of composite materials was carried out with the standard triple test modes in size of 7.07 cm × 7.07 cm × 7.07 cm at room temperature with tap water for pulping. Each of the indicators was made of 6 test blocks, which curied in a certain environment that the temperature is 20 ℃ and the humidity is more than 93% after demoulding. When the activation time was over, samples should be taken to have a strength test in the rigid hydraulic Instron 250 kN servo material testing machine for the purpose of getting the values of the uniaxial compressive strength, filling ratio, and concentration at different curing time. Through the strength test that strength value's range was 1.46 MPa to 2.78 MPa, we ensure the ratio range as Fly ash: Slag: Phosphogypsum equals 1:1:4.7 to 1:1:8, the content of qucklime was 8%, and the concentration of composite cementitious materials was 63%.

3. **Activity characteristics of the composite cementitious materials**

3.1. *Experiment design of activity characteristics*

Among evaluations of chemical activity effect about the silicon aluminium cementitious material, the method of K_a value[7] proposed by Huizhen Lian was widely used. This method can accurately obtain relativity between the activity index of volcanic ash and the soluble SiO_2 and Al_2O_3 in fly ash by determining the content of active SiO_2 and Al_2O_3 in fly ashes. This project tests was carried out mainly with reference to the K_a value method, and then was considered the influence of temperature, activation time and material fineness to the law of exsolution of active SiO_2 and Al_2O_3 in the phosphogypsum composite cementitious material. The designs are shown in Table 2.

Table 2. Experimental design of the activity characteristics of phosphogypsum composite cementitious materials in the environment of saturated lime water

NO.	Phosphogypsum composite(g)	Saturated lime water(ml)	Temperature (°C)	Activation time(d)	Fineness (m^2/kg)
A-1	0.5	200	20	3	PC:360
A-2	0.5	200	20	7	PC:360
A-3	0.5	200	20	14	PC:360
A-4	0.5	200	20	28	PC:360
A-5	0.5	200	20	90	PC:360
T-1	0.5	200	20	1	PC:360
T-2	0.5	200	80	1	PC:360
T-3	0.5	200	120	1	PC:360
T-4	0.5	200	200	1	PC:360
F-1	0.5	200	20	1	PC:360
F-2	0.5	200	20	1	PC:400
F-3	0.5	200	20	1	PC:450
F-4	0.5	200	20	1	PC:475

Notice:1. It is the same ratio of No. A、F、T and is easy for data processing analysis with different number. The proportion of composite bindes was that Fly ash: Slag : Phosphogypsum=1 : 1 : 7 ;

2.The formula for determing the fineness was that: $\mathbf{F} = \frac{\mathbf{A0.15 + A0.3 + A0.6 + A1.18 + A2.36 + A4.75}}{\mathbf{100}}$

F -Fineness modulus, A0.15- Cumulative percentage of the grain which size is bigger than 0.15mm.

3.2. *Analysis* of *activity characteristics*

$$\begin{cases} S_T = [(f_{PC,\,SiO_2} + f_{PC,\,Al_2O_3}) \times 500\text{mg} / 0.25\text{L}] \\ K_\alpha = \dfrac{f_{D,SiO_2} + f_{D,Al_2O_3}}{S_T}\,\% \end{cases} \tag{1}$$

By formula (1), it was respectively known that the total amount of dissolution SiO2, Al2O3: ST=4067.4(mg/L)；

By formula (1), it was respectively known that the activity Al-Si’s dissolution and Ka of composite cementitious materials, which was shown in Table 3.

Table3. The Activity Al-Si's Dissolution and K_a of phosphogypsum composite cementitious materials

No.	Activity Al_2O_3 (mg/L)	Activity SiO_2 (mg/L)	Value K_a
A-1	106.24	201.3	7.56%
A-2	122.7	314.72	10.75%
A-3	154.68	409.24	13.86%
A-4	249.4	429.74	16.70%
A-5	212.36	694.7	22.30%
T-1	101.35	189.65	7.15%
T-2	254.56	741.73	24.49%
T-3	274.1	759.08	25.40%
T-4	103.44	189.38	7.20%
F-1	108.37	199.76	7.58%
F-2	106.73	201.04	7.57%
F-3	107.56	203.4	7.65%
F-4	106.09	202.79	7.59%

3.2.1 Analysis of the fineness factor

The figure 1 that represents the composite binder's K_a value of different fineness in the alkaline environment of 20 ℃ shows the K_a value of composite materials was not significantly increased with decreasing of the fineness, mainly because that:

(1) As composite cementitious materials contain small amounts of soluble phosphorus and fluorine and other harmful substances, resulting in the setting time of composite materials up to nearly 15 hours and inhibiting the free diffusion of activity SiO_2, Al_2O_3.

(2)The experiment mainly studies the activity characteristics of composite materials that a certain fineness of those can adequate response with OH^- , which shows the evaluation of K_a value possesses certain applicability and limitation for the activity characteristics of inorganic silicon aluminum materials.

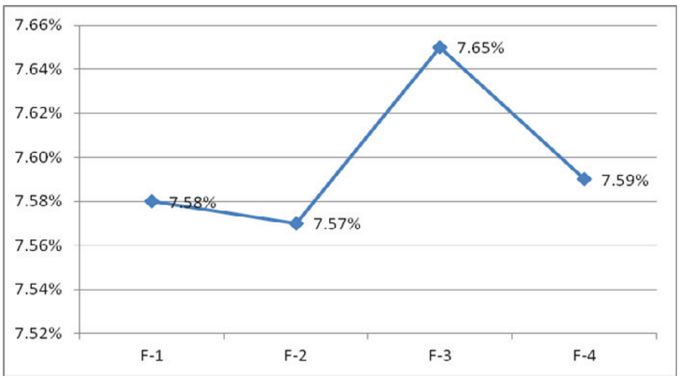

Fig.1. Composite binder's K_a values of different fineness in the alkaline environment of 20℃

3.2.2 Analysis of the activation time factor

The figure 2 that represents the composite binder's K_a value of different activation time in the alkaline environment of 20℃ shows the K_a value of composite materials increases slowly between 3 days and 28 days but increases more quickly between 28 days and 90 days, mainly because that:

(1) Before the 28 activation days, the reactions among the composite materials mainly appear the physical filling property. Because of the close relationship between the Si-O and Al-O bond cleavage and the density of OH^-, there appears a layer of barrier film inhibiting network aggregation of the Si-O-Al on the surface of the composite materials as time goes when the density of OH^- in the solution is higher than that in the pore. In other words, the C-S-H and C-A-H materials formed by the reaction between unsaturated bond and $Ca(OH)_2$ that hydration products of CaO delay the invasion of the reaction medium in the composite materials.

(2) After the 28 activation days, for ash effect occurred among the composite materials, in the alkaline environment, the amount of free ions in the reaction process was significantly increased causing the density of OH^- in the pore is higher than that in the solution, accelerating the dissolution, diffusion and transfer of the activity SiO_2 and $A1_2O_3$, at the same time reducing the thickness of the barrier film and also improving the dissolution rate.

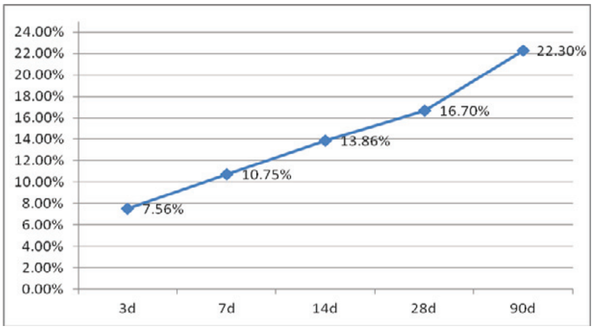

Fig.2. Composite binder's Ka values of different activation time in the alkaline environment of 20℃

3.2.3 Analysis of the temperature factor

The figure 3 that represents the composite binder's K_a value of different temperature in the alkaline environment shows the K_a value of composite materials increases sharply between 20 ℃ and 80 ℃ but increases more slowly between 80 ℃ and 120 ℃. The reason that K_a value suddenly become smaller showing a inflection trend at the temperature 200 ℃ was that:

(1) Within a certain range, temperature can accelerate the reaction rate among composite cementitious materials and destroy the network structure of vitreous body from 80 ℃ to 120 ℃, thereby speeding up the reaction of dissolution, diffusion and transfer of activity SiO_2, Al_2O_3.

(2) For the reason that there exists a certain temperature limit of substance on its own activity, the high temperature will reduce the activity itself that is not conductive to dissolution of the activity SiO_2, Al_2O_3, therefore, the optimal reaction temperature of the composite materials was 80 ℃.

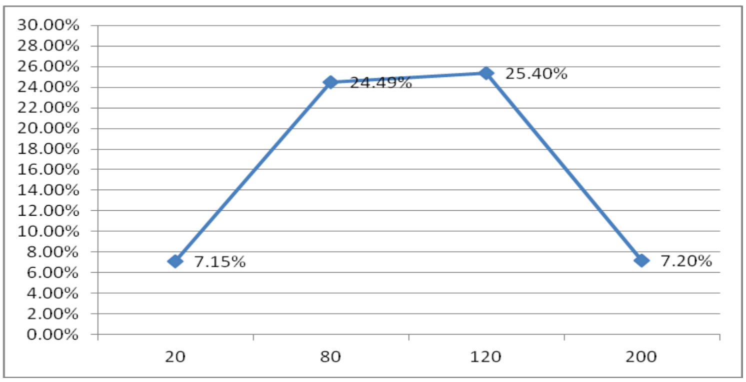

Fig.3. Composite binder's Ka values of different temperature in the alkaline environment

3.2.4 Comprehensive analysis of all factors

The figure 4 represents that the composite binder's Ka value trends in different alkaline environment. For fineness, Ka value of the composite materials was not increasing significantly as long as the reducing of fineness, which indicating less relationship of dissolution of the activity Al_2O_3 and SiO_2 affected by fineness factor. For activation time, the composite binder's K_a value not only increased more significantly than the condition of fineness but also increased quickly as long as growing of activation time. For temperature, for the reason that temperature can speed up reaction of dissolution, diffusion and transfer of activity SiO_2, Al_2O_3 among composite cementitious materials and destroy the network structure of vitreous body, it is the most obvious affected by the temperature on composite materials. In summary, the degree of activity features affected by the external environment was followed by Temperature>Activation time>Fineness.

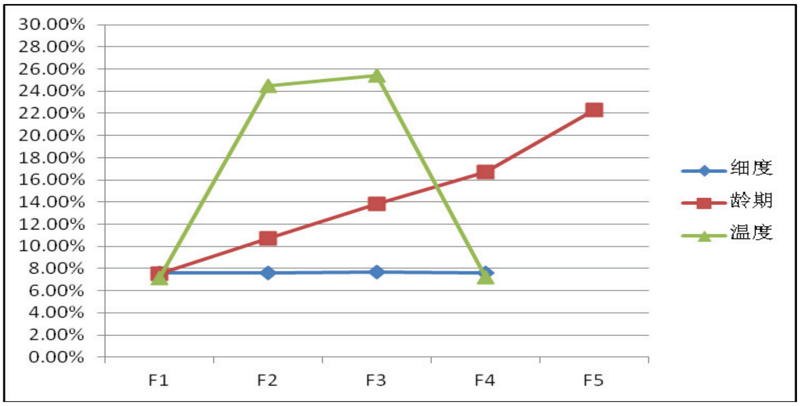

Fig.4. Composite binder's Ka values trends graph in different alkaline environment

4. **Conclusion**

By determination of physical and chemical properties and analysis of activity characteristics about composite cementitious materials, it provides a theoretical guidance for the large-scale industrial application with solid emissions like phosphogypsum, mainly conclude that:

(1) phosphogypsum cannot stand alone as filling aggregate while can be changed by means of mixing fly ash, slag and activator with phosphogypsum. Through the strength test that strength value's range was 1.46 MPa to 2.78 MPa, we ensure the ratio range as Fly ash: Slag: Phosphogypsum equals 1:1:4.7 to 1:1:8, the content of quicklime was 8%, and the concentration of composite cementitious materials was 63%.

(2) Studied and analyzed the influence affected by the fineness, activation time and temperature on the activity characteristics of the composite cementitious materials. For fineness, as composite cementitious materials contain small amounts of soluble phosphorus and fluorine and other harmful substances, resulting in the setting time of composite materials up to nearly 15 hours and inhibiting the free diffusion of activity SiO_2, Al_2O_3. For activation time, there is an inflection point of composite materials at the 28th day, showing the relationship between K_a value and density of OH^- in the alkaline environment. There appears a layer of barrier film inhibiting network aggregation of the Si-O-Al on the surface of the composite materials as time goes when the density of OH^- in the solution is higher than that in the pore, on the contrary, accelerate the dissolution, diffusion and transfer of the activity SiO_2 and $A1_2O_3$ when the density of OH^- in the pore is higher than that in the solution. For temperature, it can speed up the rate of dissolution, diffusion and transfer of the activity SiO_2 and $A1_2O_3$ by means of accelerating the reaction rate and destroy the network structure of vitreous body about composite materials, however too high temperature will reduce the activity of substance on its own.

(3) By comparing, the degree of activity features affected by the external environment was followed by Temperature>Activation time>Fineness.

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